

General Methods

NMR spectra were recorded on Bruker Avance 300 (300 MHz). Chemical shifts (ppm) are given relative to solvent: references for CDCl₃ were 7.26 ppm (¹H-NMR) and 77.0 ppm (¹³C-NMR). ¹³CNMR spectra were acquired on a broad band decoupled mode. Multiplets were assigned as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), m (multiplet) and br. s (broad singlet). All measurements were carried out at room temperature unless otherwise stated. Gas chromatography analysis was performed on an Agilent HP-5890 instrument with a FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d., 0.25 µm film thickness) using argon as carrier gas. The products were isolated from the reaction mixture by column chromatography on silica gel 60, 0.063-0.2 mm, 70-230 mesh (Merck).

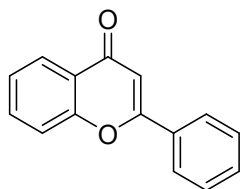
All reactions were carried out under air atmosphere. All the reagents were purchased from Sigma-Aldrich or Alfa-Aesar chemical company.

Typical reaction procedure for the carbonylative synthesis of flavone: 10 % Pd/C (1 mol %; 2.5 mg), 2-iodophenol (0.25 mmol), ethynylbenzene (0.3 mmol), diethylamine (0.5 mmol) and toluene (1 mL) were transferred into a vial (5 mL reaction volume) equipped with a septum, a small cannula and a stirring bar. Then, the vial was placed in an alloy plate, which was transferred into a 300 mL autoclave of the 4560 series from Parr Instruments® under air atmosphere. After flushing the autoclave three times with CO, a pressure of 20 bar was adjusted and the reaction was performed for 20 hours at 110°C. After the reaction, the autoclave was cooled down to room temperature and the pressure was released carefully. The crude product was purified by column chromatography using pentane/AcOEt (5:1) as eluent.

Procedure for Catalyst Recycling

The catalyst obtained after filtration was thoroughly washed with distilled water (3-5 mL) and then with methanol, ethyl acetate and acetone (3-5 mL) to remove any traces of organic material if present. The resulting catalyst was dried and was then used for the next cycle.

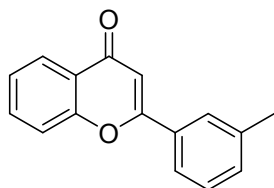
2-Phenyl-4*H*-chromen-4-one



¹H NMR (300 MHz, Chloroform-*d*) δ 8.24 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.98-7.88 (m, 2H), 7.70 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H), 7.62-7.49 (m, 4H), 7.48-7.36 (m, 1H), 6.85 (s, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 178.47, 163.49, 156.28, 133.83, 131.76, 131.65, 129.06, 126.32, 125.71, 125.27, 123.91, 118.10, 107.56.

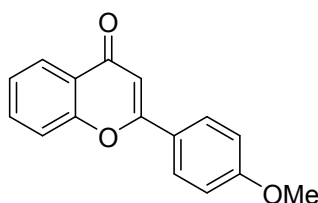
2-(*m*-Tolyl)-4*H*-chromen-4-one



¹H NMR (300 MHz, Chloroform-*d*) δ 8.21 (ddd, *J* = 8.0, 1.7, 0.5 Hz, 1H), 7.74-7.63 (m, 3H), 7.56 (ddd, *J* = 8.4, 1.1, 0.5 Hz, 1H), 7.44-7.30 (m, 3H), 2.44 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 178.49, 163.66, 156.28, 138.86, 133.77, 132.46, 131.70, 128.96, 126.86, 125.68, 125.21, 123.95, 123.53, 118.13, 107.51, 21.55.

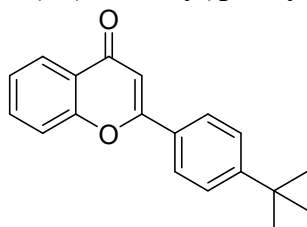
2-(4-Methoxyphenyl)-4*H*-chromen-4-one



¹H NMR (300 MHz, Chloroform-*d*) δ 8.13 (dt, *J* = 7.9, 1.3 Hz, 1H), 7.85 – 7.73 (m, 2H), 7.59 (ddt, *J* = 8.6, 7.1, 1.4 Hz, 1H), 7.45 (dt, *J* = 8.5, 1.2 Hz, 1H), 7.32 (ddt, *J* = 8.1, 7.1, 1.2 Hz, 1H), 6.98-86 (m, 2H), 6.66 (s, 1H), 3.79 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 178.37, 163.44, 162.42, 156.17, 133.61, 128.02, 125.64, 125.11, 123.96, 123.88, 117.99, 114.47, 106.12, 55.54.

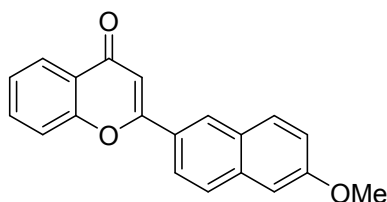
2-(4-(*tert*-Butyl)phenyl)-4*H*-chromen-4-one



¹H NMR (400 MHz, Chloroform-*d*) δ 8.13 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.58 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H), 7.50 – 7.36 (m, 3H), 7.34 – 7.25 (m, 1H), 6.71 (s, 1H), 1.27 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 178.44, 163.59, 156.26, 155.34, 133.68, 128.91, 126.15, 126.06, 125.67, 125.14, 124.01, 118.09, 107.07, 35.05, 31.15.

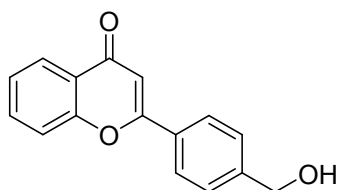
2-(6-Methoxynaphthalen-2-yl)-4*H*-chromen-4-one



¹H NMR (300 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 1.4 Hz, 1H), 8.13 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.80 -7.44 (m, 5H), 7.31 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 7.16-7.00 (m, 2H), 6.79 (s, 1H), 3.84 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 178.43, 163.55, 159.38, 156.27, 136.26, 133.72, 130.62, 128.31, 127.63, 126.69, 126.50, 125.67, 125.16, 123.98, 123.09, 120.02, 118.08, 107.10, 105.77, 55.46.

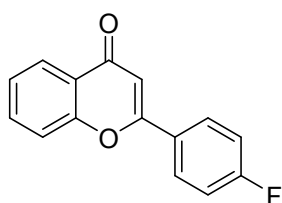
2-(4-(Hydroxymethyl)phenyl)-4*H*-chromen-4-one



^1H NMR (300 MHz, $\text{MeOD-}d_1$) δ 6.82 (d, $J = 8.0$ Hz, 1H), 6.70 (d, $J = 8.1$ Hz, 2H), 6.56-6.46 (m, 1H), 6.44-6.37 (m, 1H), 6.28-6.07 (m, 3H), 3.39 (s, 2H).

^{13}C NMR (75 MHz, MeOD) δ 179.07, 164.26, 156.20, 145.97, 134.22, 129.82, 126.83, 126.10, 125.24, 124.59, 123.01, 118.01, 105.86, 62.97.

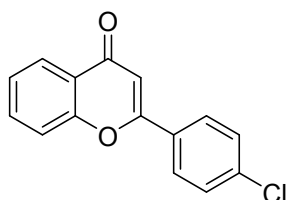
2-(4-Fluorophenyl)-4*H*-chromen-4-one



^1H NMR (300 MHz, $\text{Chloroform-}d$) δ 8.13 (d, $J = 7.9$ Hz, 1H), 7.90-7.78 (m, 2H), 7.68-7.56 (m, 1H), 7.47 (d, $J = 8.5$ Hz, 1H), 7.34 (t, $J = 7.5$ Hz, 1H), 7.23-7.06 (m, 2H), 6.69 (s, 1H).

^{13}C NMR (75 MHz, CDCl_3) δ 178.70, 164.77 (d, $J = 253.1$ Hz), 162.43, 156.17, 133.90, 128.53 (d, $J = 8.9$ Hz), 127.95 (d, $J = 3.3$ Hz), 125.73, 125.36, 123.87, 118.04, 116.3 (d, $J = 23.0$ Hz), 107.34.

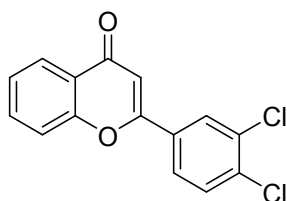
2-(4-Chlorophenyl)-4*H*-chromen-4-one



^1H NMR (300 MHz, $\text{Chloroform-}d$) δ 8.22 (dd, $J = 7.9, 1.6$ Hz, 1H), 7.86 (d, $J = 7.3$ Hz, 2H), 7.76-7.64 (m, 1H), 7.41 (dd, $J = 8.0, 1.0$ Hz, 4H), 6.80 (s, 1H).

^{13}C NMR (75 MHz, CDCl_3) δ 178.30, 162.29, 156.18, 137.95, 133.99, 130.22, 129.42, 127.58, 125.77, 125.44, 123.88, 118.08, 107.67.

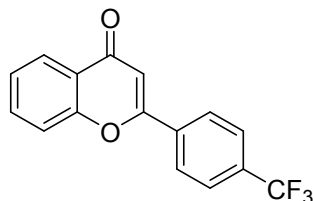
2-(3,4-Dichlorophenyl)-4*H*-chromen-4-one



^1H NMR (300 MHz, $\text{Chloroform-}d$) δ 8.20-8.10 (m, 1H), 7.96 (d, $J = 2.1$ Hz, 1H), 7.72-7.60 (m, 2H), 7.59-7.46 (m, 2H), 7.37 (ddd, $J = 8.1, 7.1, 1.1$ Hz, 1H), 6.72 (s, 1H).

^{13}C NMR (75 MHz, CDCl_3) δ 178.11, 160.92, 156.11, 136.01, 134.18, 133.73, 131.68, 131.16, 128.10, 125.81, 125.62, 125.31, 123.85, 118.11, 108.18.

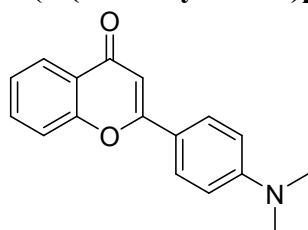
2-(4-(Trifluoromethyl)phenyl)-4*H*-chromen-4-one



¹H NMR (400 MHz, Chloroform-*d*) δ 8.21 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 2H), 7.80 – 7.66 (m, 3H), 7.60 – 7.53 (m, 1H), 7.47 – 7.38 (m, 1H), 6.84 (s, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 178.15, 161.59, 156.20, 135.19, 134.13, 133.14(q, *J* = 32.6 Hz), 126.65, 126.05(q, *J* = 3.8 Hz), 125.79, 125.56, 123.93, 123.63(q, *J* = 271.6 Hz), 118.14, 108.73.

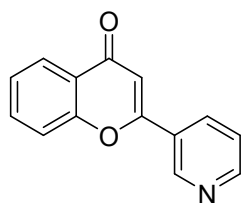
2-(4-(Dimethylamino)phenyl)-4*H*-chromen-4-one



¹H NMR (400 MHz, Chloroform-*d*) δ 8.13 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.76-7.67 (m, 2H), 7.56 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H), 7.47-7.39 (m, 1H), 7.32-7.25 (m, 1H), 6.67- 6.62 (m, 2H), 6.60 (s, 1H), 2.97 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 178.26, 164.31, 156.16, 152.46, 133.17, 127.70, 125.54, 124.76, 124.07, 118.20, 117.85, 111.62, 104.37, 40.08.

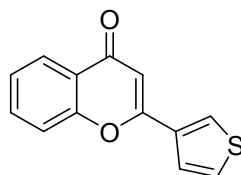
2-(Pyridin-3-yl)-4*H*-chromen-4-one



¹H NMR (300 MHz, Chloroform-*d*) δ 9.17 (d, *J* = 2.3 Hz, 1H), 8.76 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.22 (dd, *J* = 8.2, 1.6 Hz, 2H), 7.77-7.66 (m, 1H), 7.62-7.53 (m, 1H), 7.53-7.38 (m, 2H), 6.84 (s, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 178.02, 161.05, 156.23, 152.23, 147.56, 134.16, 133.59, 127.89, 125.83, 125.61, 123.95, 123.76, 123.38, 118.14, 108.45.

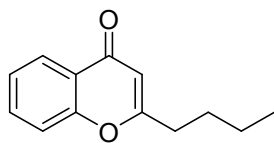
2-(Thiophen-3-yl)-4*H*-chromen-4-one



¹H NMR (300 MHz, Chloroform-*d*) δ 8.22 (dd, *J* = 8.0, 1.8 Hz, 1H), 8.02 (d, *J* = 2.1 Hz, 1H), 7.79-7.66 (m, 2H), 7.66-7.53 (m, 2H), 7.44 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 6.79 (s, 1H).

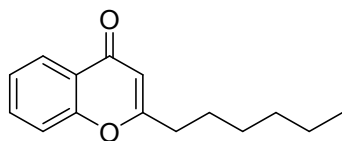
¹³C NMR (75 MHz, CDCl₃) δ 178.11, 160.92, 156.11, 136.01, 134.18, 131.16, 128.10, 125.81, 125.62, 125.31, 123.85, 118.11, 108.18.

2-Butyl-4*H*-chromen-4-one



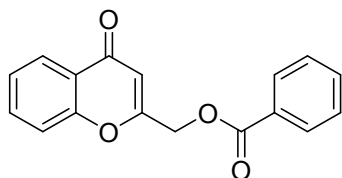
^1H NMR (400 MHz, Chloroform-*d*) δ 8.18 (dd, $J = 7.9, 1.7$ Hz, 1H), 7.63 (dd, $J = 7.1, 1.6$ Hz, 1H), 7.46-7.33 (m, 2H), 6.19 (s, 1H), 2.67- 2.58 (m, 2H), 1.77-1.66 (m, 2H), 1.42 (dd, $J = 14.8, 7.4$ Hz, 2H), 0.96 (t, $J = 7.3$ Hz, 3H).
 ^{13}C NMR (101 MHz, CDCl_3) δ 178.34, 169.84, 156.57, 133.42, 125.69, 125.07, 124.90, 117.88, 109.86, 34.08, 28.89, 22.15, 13.76.

2-Hexyl-4*H*-chromen-4-one



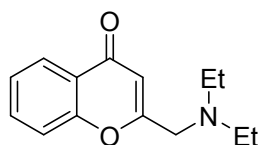
^1H NMR (300 MHz, Chloroform-*d*) δ 8.11 (dd, $J = 8.0, 1.7$ Hz, 1H), 7.57 (ddd, $J = 8.6, 7.1, 1.7$ Hz, 1H), 7.42-7.25 (m, 2H), 6.12 (s, 1H), 2.55 (t, $J = 7.6$ Hz, 2H), 1.67 (p, $J = 7.3$ Hz, 2H), 1.42-1.15 (m, 6H), 0.91-0.76 (m, 3H).
 ^{13}C NMR (75 MHz, CDCl_3) δ 178.44, 169.92, 156.53, 133.45, 125.67, 124.91, 123.71, 117.87, 109.80, 34.37, 31.48, 28.69, 26.79, 22.53, 14.07.

(4-Oxo-4*H*-chromen-2-yl)methyl benzoate



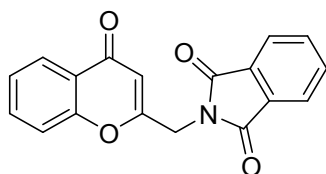
^1H NMR (300 MHz, Chloroform-*d*) δ 8.15 (ddd, $J = 25.6, 8.3, 1.6$ Hz, 3H), 7.74-7.55 (m, 2H), 7.54-7.35 (m, 4H), 6.49 (s, 1H), 5.27 (s, 2H).
 ^{13}C NMR (75 MHz, CDCl_3) δ 177.94, 165.54, 162.79, 156.24, 134.01, 133.78, 129.93, 128.88, 128.66, 125.84, 125.46, 123.98, 118.06, 109.89, 61.97.

2-((Diethylamino)methyl)-4*H*-chromen-4-one



^1H NMR (300 MHz, Chloroform-*d*) δ 8.19 (dd, $J = 8.0, 1.7$ Hz, 1H), 7.71-7.58 (m, 1H), 7.50-7.32 (m, 2H), 6.47 (s, 1H), 3.57 (s, 2H), 2.66 (q, $J = 7.1$ Hz, 4H), 1.09 (t, $J = 7.1$ Hz, 6H).
 ^{13}C NMR (75 MHz, CDCl_3) δ 178.43, 169.97, 156.47, 133.51, 125.74, 125.03, 124.05, 118.07, 110.63, 55.04, 47.71, 12.07.

2-((4-Oxo-4*H*-chromen-2-yl)methyl)isoindoline-1,3-dione



^1H NMR (300 MHz, Chloroform-*d*) δ 8.12 (dd, $J = 8.0, 1.7$ Hz, 1H), 7.88 (ddd, $J = 12.9, 5.5, 3.0$ Hz, 2H), 7.75 (ddd, $J = 12.4, 5.5, 3.1$ Hz, 2H), 7.63 (ddd, $J = 8.7, 7.1, 1.7$ Hz, 1H), 7.50-7.28 (m, 2H), 6.22 (s, 1H), 4.81 (s, 2H).

^{13}C NMR (75 MHz, CDCl_3) δ 177.83, 167.23, 162.21, 156.24, 134.61, 134.37, 133.91, 131.75, 125.77, 125.45, 123.87, 118.07, 109.58, 39.02.

